

[Second Edition.]

BRITISH PATENT OFFICE

PATENT SPECIFICATION

458,839



Convention Date (United States) : June 21, 1934.

Application Date (in United Kingdom) : June 21, 1935. No. 17940 / 35.

Complete Specification Accepted : Dec. 21, 1936.

COMPLETE SPECIFICATION

Chitin Compounds.

We, E. I. DU PONT DE NEMOURS AND Co., a corporation organised and existing under the laws of the State of Delaware, United States of America, located at 5 Wilmington, State of Delaware, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained 10 in and by the following statement :—

This invention relates to processes for the treatment of polymeric amino carbohydrate derivatives. Specifically it relates to the treatment of chitin and 15 chitin-like materials.

Chitin is a polymeric acetamino derivative of a carbohydrate. It occurs in the shells of various crustacea and has been recognised to have a structure related to 20 that of cellulose, wherein in place of the glucose building stone of the cellulose, the building stone is chitosamine in the form of the acetyl derivative. Wester reviews the subject in Archiv der Pharmazie 247 25 282—307 (1909).

A material known as chitosan has been prepared by heating chitin with 50% aqueous potassium hydroxide at 160° C. or above. These conditions are, it has now 30 been found, too drastic to obtain an undegraded deacetylated chitin. Further the literature on the subject is silent on the action of oxygen or oxidising agents upon chitin or chitosan to form degradation 35 products.

This invention has as an object the preparation of substantially undegraded deacetylated chitin.

According to the invention we manufacture 40 substantially undegraded, at least partially deacetylated chitin by treating chitin, preferably under limited access of air, with 5—55% aqueous caustic alkali at a temperature not exceeding 150° C. 45 until the product is soluble in dilute aqueous acetic acid to give solutions which, at a concentration of 2.5 parts of product per 100 parts of dilute aqueous acetic acid have a viscosity greater than 50 1 poise at 25° C.

The invention is carried into practical effect by use of aqueous caustic alkali solutions of concentrations of from 5 to

55% by weight. The time and temperature of reaction are adjusted in accord 55 with the caustic alkali concentration adopted. In general the higher the concentration of caustic alkali, the lower the temperature and/or the shorter the time of the deacetylation treatment. Thus, when 5% caustic soda is used at 150° C. about 24 hours are required to reach a soluble stage of deacetylation. With 50% caustic soda at 100° C. only about one hour is necessary to reach the same result. With 40% caustic soda at 100° C. about 18 hours are required to reach the same degree of deacetylation as in the above two instances. In any event the alkaline treatment is continued until the product 60 is soluble in dilute acetic acid, and is discontinued before the product becomes degraded to a substantial degree and by this is meant that the treatment is discontinued before the reaction has proceeded to the point where the nucleus of the hexose amine polymer is broken down to such an extent that a continuous film 65 can no longer be obtained from the solution of the product in dilute acetic acid. Chitin from different sources has been 70 found to vary somewhat in sensitiveness to alkaline reagents and therefore conditions are controlled during deacetylation avoiding conditions so drastic as to cause 75 any substantial evolution of ammonia or degradation of the hexose amine polymer. 80

By way of explanation of the invention it can be said here that the extent to which chitin is deacetylated by means of aqueous caustic alkali is probably governed by the following factors; caustic concentration, temperature of deacetylation, time of contact with the caustic, previous treatment of the chitin, particle size, and finally, the density of the chitin. While these factors appear to be very closely interrelated, the following generalisations may be drawn. First, holding all other 90 factors constant, an increase in caustic concentration increases the extent to which deacetylation is carried. Second, for each definite caustic concentration an increase in temperature, other factors 95 being constant, increases the extent to 100 105

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which deacetylation is carried. Third, at a given caustic concentration and temperature, other factors being constant, an increased time of reaction increases the extent of deacetylation. In other words, it is believed that there is no appreciable reverse reaction involved. Fourth, any previous treatment of the chitin which renders it more accessible to the caustic will undoubtedly increase the extent of deacetylation at a given caustic concentration, temperature, and time of contact, although it is very difficult to differentiate this factor from that of particle size and density. Fifth, the particle size of the chitin which is used governs largely the area which is available to the caustic and hence the rate at which the caustic penetrates the particles, thus causing deacetylation to depend, at a given caustic concentration and temperature, other factors being constant, upon the particle size. Sixth, the density of the chitin particles influences the rate at which the caustic penetrates, hence, regulates the extent to which deacetylation takes place, other factors being constant.

Chitin obtained by the purification or cleansing of any of the ordinary chitin-containing raw materials may be used. These latter include the shells of shrimps, crabs, lobsters and other crustacea. The waste from certain canning industries is a very suitable source of such raw materials. Insects such as beetles, grasshoppers, locusts and the like and fungi such as aspergillus niger, mushrooms and the like also provide sources of chitin, but the shells of crustacea are preferred as raw materials.

In cleansing these to provide chitin for the purposes of the invention, the method of purification adopted depends chiefly upon the type of raw material used and upon the amount and character of the foreign matter such as protein and other impurities to be removed. Moreover, the quantities and types of detergents used will be determined largely by the quantity of protein materials to be removed. Thus, for some batches of "shrimp meal" it is advantageous to use caustic soda in place of soda ash while for the usual type of "crab backs" an even milder detergent than 1% soda ash may be used. Thus, the quantity, concentration, and type of detergent used may be varied according to the needs of the particular raw material used. In place of soda ash, trisodium phosphate or caustic soda, or other agents capable of rendering proteinous materials soluble may be used. It is thus possible to use sodium sulphide, sodium sulphite, sodium bisulphite, calcium bisulphite, potassium carbonate, sodium bicarbonate,

potassium bicarbonate, potassium hydroxide, calcium hydroxide, copper ammonium solution, sodium silicate, sulphurous acid and certain putrificative bacteria as agents in removing the adhering proteins from the chitin. In general, agents capable of exerting a peptising action on proteinous materials are suitable for use in separating chitin from the other constituents present in the raw material. In the special case of the use of certain fungi as raw materials it may be desirable to separate chitin from cellulose. This may be done with copper-ammonium or sodium thiocyanate solutions or by xanthation or other means by which cellulose is rendered soluble while chitin is unaffected.

The quantity and type of acid used to remove lime and other inorganic salts may vary with the type of raw materials. Thus, use may be made of hydrochloric acid of about 0.875% concentration. However, if a counter-current system is used, an acid of lower concentration may be employed in the first treatment, where acid of higher concentration is used in the final treatment to remove the last traces of inorganic salts. Other inorganic acids forming soluble calcium salts, such as nitric acid, sulphurous acid, and other inorganic acids or organic acids such as acetic and formic may be used in place of hydrochloric acid to remove lime.

The order in which the acid and alkaline purification treatments are employed may be varied, the order depending to a considerable extent upon the type of raw material used. Thus, in case large quantities of water soluble materials are present it is more economical to give a dilute alkaline treatment followed by acid since the acid may thus be used exclusively to remove lime rather than be used up in reacting somewhat with the protein material present. If, on the other hand, the raw materials consist of the comparatively clean "crab backs" the acid treatment may be given first, since lime is the essential ingredient to be removed in this case.

No bleaching step will be found necessary in case the acid and alkali treatment is carried out properly. In case, however, that it is desired to bleach the chitin a dilute solution of potassium permanganate, sodium hypochlorite, or sulphur dioxide, or a solution of sodium hydrosulphite, sodium bisulphite or other mild bleaching agent may be used. In general, however, no bleaching agent is required.

The treatment of the shells with alkali is continued only until the proteinous material has all been loosened and made

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water soluble. The acid treatment is continued only until all the lime has been removed and made water soluble. Washing with water after each step is, of course, advisable. The temperature at which the alkaline treatment is given may vary, but a temperature of about 100° C. is preferred because of the economy of time, convenience of operation, etc. By the use of pressure equipment the time of reaction may be shortened. The temperatures of acid treatment may likewise be varied from 0 to 100° C. although temperatures of about 25° C. are more economical of chitin. The most favourable temperature depends considerably upon the acid used to remove the lime salts. The concentration of the acid used may vary from a few parts per million to a concentrated acid. The use of concentrations of about 5% for the final acid treatment and of about 1 to 1½% hydrochloric acid for the first treatment has been found economical of chitin.

By way of detailed description of the manner in which purified chitin is made from suitable raw materials the following is given:—

**EXAMPLE 1.**

In an earthenware crock provided with a false bottom were placed 25000 parts of shrimps "heads and hulls". The shells were covered with 200,000 parts of water to which had been added 900 parts of soda ash and 18 parts of a mixture of sodium salts of sulphate esters of C<sub>8</sub> to C<sub>18</sub> primary alcohols mainly lauryl. Direct steam heat was applied for about four hours. The water was then drained off, the shells washed with fresh water and the soda ash treatment repeated. This left the shells free from adhering meat and almost pure white. After washing free from alkali the shells were covered with 200,000 parts of water containing 5000 parts of 35% hydrochloric acid and left over night. The next morning the acid was drained off and the shells washed repeatedly with fresh water to remove all adhering salts. Finally the chitin was given an alkali boil with 900 parts of soda ash and 18 parts of a good textile soap in 200,000 parts water. This treatment left the chitin in a pure white condition. After washing with fresh water until neutral to phenolphthalein, the chitin was dried at 65° C. in an air dryer. Yield 5670 parts of 22½% based on the dry weight of the shells. 25 parts of chitin were then treated with substantial exclusion of air at 115° C. during six hours with 1200 parts of 40% sodium hydroxide. At the end of this time the caustic was drained off and the shells washed with water until neutral to phenolphthalein. After drying at 65°

C. the yield was 20 parts of deacetylated chitin containing about 0.82 free amine groups per chitosamine residue.

161 parts of deacetylated chitin prepared as above were mixed with 48 parts of acetic acid and 3981 parts of water. After stirring to complete solution the mixture was filtered through an appropriate filter. The viscosity of the solution thus prepared was approximately 600 poises. By running the solution on a glass plate and evaporating to dryness films were obtained having a tensile strength of approximately 9000 lbs. per square inch.

**EXAMPLE 2.**

Chitin (preferably cleaned as described) is heated for 1 hour at 100° C. under limited access of air with 500% sodium hydroxide in the proportions of 1 part chitin to 10 parts sodium hydroxide solution. The product is then washed free from alkali and dried. The deacetylated chitin thus obtained is completely soluble in dilute acetic acid and contains about 0.82 free amine groups per chitosamine residue. A 5% solution of this deacetylated chitin in 1½% acetic acid had a viscosity of approximately 2800 poises.

The viscosity of this solution may be modified if desired, as follows. 10 parts of a hydrogen peroxide solution containing 0.019% H<sub>2</sub>O<sub>2</sub> are added. After thoroughly mixing, the solution is heated at 50° C. during four hours. After cooling to room temperature the product has a viscosity of about 5.2 poises. The solution thus obtained may be used as a sizing material, as a film-forming material, and in preparing filaments.

**EXAMPLE 3.**

In order to approach complete deacetylation, the following method is recommended. One part of pure chitin obtained as above is intimately mixed with 10 parts of 50% sodium hydroxide in a vessel suitable for the essential exclusion of air. The mixture is then heated to 100° C. for 48 hours with stirring, air being excluded. At the end of this time, the product is isolated in the usual manner. The product prepared as described approaches complete deacetylation.

Free access of oxygen to the chitin during the deacetylation step has a substantial degrading effect on the deacetylated chitin obtained. Therefore during the deacetylation step the reaction is preferably carried out with a limited access of air as by the use of closed vessels or vessels in which the surface of the reaction mixture exposed to air is low as compared with the volume of the reaction

mixture. Thus in a cylindrical reaction vessel where the diameter of the exposed surface is not more than the depth of the reaction mixture, a sufficiently limited access of air is secured. In stirring the surface is not often renewed. The following tables illustrate the effect of time, temperature and caustic concentration upon the properties of deacetylated chitin as measured by viscosity, solubility, and tensile strength of films prepared from the solution, all of which properties are influenced markedly by degradation of the chitin molecule.

15 TABLE I  
Effect of time on the Quality of Deacetylated Chitin Prepared with 50.9% NaOH at 100° C. using 20—40 mesh Crab Chitin.

20	No.	Chitin (parts)	NaOH Soln. (parts)	Time (hrs)	Viscosity 5% Soln. (poises)	Tensile Strength of films. Lbs. per sq. in.
1	5	50		1	630	9625
2	5	50		2.5	63	8200
3	5	50		6.0	46	8140
25	4	5	50	16.0	36	7620
	5	5	50	48.0	11	8250

30 TABLE II  
Effect of Time on the Preparation of Deacetylated Chitin by Means of 39.1% NaOH at 100° C. using 20—40 mesh Crab Chitin.

30	No.	Chitin (parts)	NaOH Soln. (parts)	Time (hrs)	Viscosity 5% Soln. (poises)	Solubility
1	5	50		2	—	Only slight
2	5	50		4	—	Highly swollen
35	3	5	50	6	—	Almost complete
	4	5	50	18	96	Good solution
	5	5	50	20	—	" "
	6	5	50	48	21.5	" "

40 Using 30% sodium hydroxide at 100° C. under the same conditions as the above experiment it was found that the threshold of solubility (completely swollen, fully transparent particles) was reached after 72 hours' heating.

45 At higher temperatures the following results were obtained:

50 TABLE III  
Effect of Using Higher Temperatures and Lower Caustic Concentrations. Chitin heated at 120° C. with 40.0% NaOH using Shrimp Chitin of 40—60 mesh.

50	No.	Chitin (parts)	NaOH Soln. (parts)	Time (hrs)	Viscosity 5% Soln. (poises)	Solubility
1	5	50		1	20	Excellent
55	2	5	50	4	21	"
	3	5	50	8	16	"
	4	5	50	16	8	"
	5	5	50	32	4.4	"

60 By way of further explanation it will be said that with 29.2% sodium hydroxide the threshold of solubility at 120° C. was reached after 32 hours. Using 20% sodium hydroxide at 140—145° C. in 24 hours the product was completely soluble 65 to give a viscosity of 0.67 poise for a 7% solution. Under the same conditions 10% sodium hydroxide gave complete solubility but the viscosity of the solution was not determined. Ammonium hydroxide 70 of 28% concentration at 140° C. for four hours did not give complete solubility.

When highly concentrated caustic solutions are used the treatment must be conducted at a lower temperature since concentrated caustic alkali at elevated temperature causes drastic changes in the chitin molecule as evidenced by ammonia evolution, water solubility of the product and the crystalline nature of the salts of the product and the low viscosity of the aqueous solutions of such salts. Such a treatment as for example heating at 160° C. with 50% aqueous potassium hydroxide results in a degraded product.

- Other caustic alkalis than sodium hydroxide may be used. Thus one may use potassium hydroxide, lithium hydroxide, calcium hydroxide, as also salts with a similar behaviour, e.g. trisodium phosphate, etc.
- Tables I, II and III also show the effect of time of heating upon the viscosity of the resulting deacetylated chitin. It will be noticed that, under specific conditions of caustic concentration and temperature, increased time of heating decreases the viscosity of the resulting deacetylated chitin.
- In Example 2 is described another method found practical for lowering the viscosity of solutions of deacetylated
- chitin made according to the invention. Other oxidising agents than hydrogen peroxide may be added to the deacetylated chitin solution. Thus chlorine, bromine, hypochlorous acid, perborates, permanganates, bichromates, oxygen, air and other oxidising agents may be added to solutions or deacetylated chitin and a reduction in viscosity is obtained corresponding to the amount of oxidising agent added. The following table illustrates the effect of hydrogen peroxide, but it is to be understood that other oxidising agents have a similar effect when used in the same oxidation equivalent quantities.

TABLE IV

	H <sub>2</sub> O <sub>2</sub> Conc. p. p. m.	Time Hours	Viscosity Sec.	Time Hours	Viscosity Sec.
35	670	1.4	5.8	5.4	1.0
	332	1.4	7.0	5.4	1.2
	168	1.3	9.2	5.4	1.5
40	82	1.3	10.9	5.4	7.1
	38	1.0	201	4.3	32.5
	20	1.0	213	4.3	80
	14.4	1.0	253	4.3	129
	9.2	1.0	283	4.3	204
45	4.8	1.0	388	4.3	342
	2.4	1.0	494	4.3	452
	0	1.0	568	4.3	510

These experiments were carried out at room temperature. With exclusion of air no further drop in viscosity was noted even after three weeks. The rate of viscosity drop is also dependent upon the temperature as well as upon the concentration of oxidising agent. In a series of experiments carried out at 50° C. the viscosity drop was similar to the series at room temperature, but the rate was very markedly accelerated.

By use of oxidising agents acting on solid deacetylated chitin made according to the invention a product giving solutions of lowered viscosity may be produced. Thus in a series of experiments carried out at room temperature using five grams of deacetylated chitin and 200 cc. of oxidising solution, the following results were obtained.

TABLE V.

	H <sub>2</sub> O <sub>2</sub> p. p. m.	Viscosity of 5% Solution (poises)	Viscosity of 5% Soln. (poises)
70	800	2.7	1.22
	400	17.8	0.94
	200	46	0.75
75	100	151	0.94
	50	282	8.85
	25	760	0.56
	0	1970	1970

In place of hydrogen peroxide other oxidising agents such as sodium peroxide,

chlorine, bromine, hypochlorous acid, perborates, permanganates, bichromates, oxygen, air and other oxidising agents may be added to solutions or deacetylated chitin and a reduction in viscosity is obtained corresponding to the amount of oxidising agent added. The following table illustrates the effect of hydrogen peroxide, but it is to be understood that other oxidising agents have a similar effect when used in the same oxidation equivalent quantities.

TABLE VI

Oxidising Agent	Viscosity of 5% Soln. (poises)
Sodium perborate	— 1.22
Sodium persulphate	— 0.94
Potassium permanganate	0.75
Hydrogen peroxide	— 0.94
Calcium hypochlorite	— 8.85
Sodium hypochlorite	— 0.56
Water	— 1970

The viscosity of the deacetylated chitin solutions may thus be decreased. It has also been observed that by suitable processes a solution of higher viscosity at the small concentration may be obtained. Thus a partially deacetylated chitin which, as the acetate in 5% aqueous solution, has a viscosity of 5 poises may, by heating the dry partially deacetylated chitin for 12

hours at 100° C. give a product which, in 5% aqueous solution, as the acetate, has a viscosity of 200—300 poises. The viscosity of this solution may be decreased as above and then again increased if so desired.

Since deacetylated chitin is essentially a highly polymeric free primary amine it

forms salts with acids. Many of these salts are water soluble. Table VII lists some of the acids whose salts of deacetylated chitin have been prepared. These salts are prepared from substantially undegraded, partly deacetylated chitin containing about .8 free amino groups per chitosamine residue.

TABLE VII  
SALTS OF DEACETYLATED CHITIN.

	Acid	Solubility of Salt in water.	Viscosity of 5% Solution in water (poises)
20	1. Acetic	Easily soluble	66
	2. Glycollic	" "	—
	3. Maleic	" "	83.6
25	4. Malonic	" "	646
	5. Succinic	Slowly "	—
	6. Oxalic	Difficultly soluble	—
	7. Phthalic	Slowly "	—
	8. Benzoic	Easily "	—
30	9. Benzenesulphonic	" "	—
	10. $\alpha$ -Bromo- <i>n</i> -butyric	" "	—
	11. $\alpha$ -Bromo- <i>n</i> -propionic	" "	—
	12. Phosphoric	Slightly "	—
	13. Phenyl glycine	" "	—
35	14. Iodo acetic	Easily "	—
	15. Sulphanilic	" "	—
	16. Formic	" "	—
	17. Di-chloroacetic	" "	—
	18. Pyruvic	" "	—
40	19. Lactic	" "	—
	20. Tartaric	" "	29
	21. Salicylic	Difficultly "	—
	22. Adipic	Easily "	71
	23. Sebacie	" "	—
45	24. Sulphonsalicylic	" "	—
	25. Citric	" "	34
	26. Maleic	" "	83.6
	27. Malic	" "	100
	28. Lauric	Very slightly soluble	—
50	29. Fumaric	Slowly soluble	—
	30. <i>o</i> -Benzoylbenzoic	Difficultly "	—
	31. Diphenic	" "	—
	32. Cinnamic	" "	—
	33. Mandelic	Easily soluble "	107
55	34. Clutamic	" "	82.8
	35. Hippuric	" "	910
	36. Furoic	" "	75.2
	37. Phenylacetic	" "	—
	38. Crotonic	" "	—
60	39. Caproic	" "	712
	40. Propionic	" "	260
	41. Butyric	" "	219
	42. Diethyl malonic	" "	—
	43. Pelargonic	Difficultly "	—
65	44. iso-Valeric	Easily "	275
	45. Glycine	Difficultly "	—
	46. Palmitic	Very slightly soluble	—
	47. Teraphthalic	Slightly soluble	—
	48. Chloracetic	Easily "	—
70	49. $\alpha$ -Chloropropionic	" "	121
	50. $\alpha$ -Chloro-isobutyric	" "	73.3
	51. Cyanuric	Very slightly soluble	—

TABLE VII—Continued.  
SALTS OF DEACETYLATED CHITIN.

	Acid	Solubility of Salt in water.	Viscosity of 5% Solution in water (poises)
5	52. Thioglycolic	Easily soluble	
	53. 3-Nitrophthalic	" "	48
	54. <i>a</i> -ido-propionic	" "	139
	55. iso-Butyric	" "	99
10	56. Naphthenic (Mol. Wt. 186)	" "	
	57. Naphthenic (Mol. Wt. 450)	" "	
	58. Pyruvic	" "	735
	59. Linoleic	Difficultly soluble	
	60. Anthranilic	Easily ..,	21.1
15	61. Furacrylic	" "	
	62. Hydroxy-iso-butyric	Difficultly ..,	113
	63. Sodium bisulphite	Slightly ..,	
	64. Boric	Slowly ..,	
20	65. Dithiocarbonic	Easily ..,	
	66. Sulphurous	" ..,	
	67. Hydrochloric	" ..,	
	68. Hydrobromic	" ..,	
	69. Hydriodic	" ..,	
	70. Hypochlorous	Slowly ..,	

25 The deacetylated chitin used in Table VII in preparing these salts was all of the same batch, hence, the viscosities recorded are comparable.

30 The solutions of the salts of the deacetylated chitin obtained according to this invention may be used in preparing formed articles such as films, filaments, caps and bands, and may be used as sizing and coating materials as disclosed in co-pending applications Nos. 17933 to 35 17939/35 (Serial Numbers 458,813—458,819).

40 The deacetylated chitin obtained according to the present invention is a substantially undegraded hexose amine polymer possessing useful properties. The alkaline treatment results in the removal of at least .2 but usually not quite all of the acetyl groups present without, however, removing any substantial proportion of the amino groups. Useful products contain, therefore, approximately from at least .2 up to about .9 free amino groups per chitosamine unit of the molecule.

45 50 The acid-soluble products obtained according to the present invention are capable of innumerable uses and show marked advantages over organic solvent soluble materials of the cellulose ester type. The process and products of the present invention are of peculiar advantage since the properties of the final product may be regulated by the conditions of purification and by the conditions under which deacetylation has been carried out.

55 60 The use of products which contain from .7 to .86 free amine groups per glucose amine residue is preferred. A product containing this quantity of free amine

groups is desirable, first, because it retains good film-forming properties; second, the viscosity of these products is easy to control; third, the products are easily soluble in dilute acids, forming solutions free from gelatinous particles; fourth, the product within these limits is easily produced on a plant scale.

70 By the term "substantially undegraded" as used in this application, is meant substantially undegraded in the same sense as is used in cellulose chemistry. That is, by substantially undegraded is meant a product which retains the properties of forming coherent films, of giving viscous solutions, and of being insoluble in water without the addition of acids. On theoretical grounds, this probably means that if one considers deacetylated chitin as a long chain polymerised glucose amine derivative, the chain lengths are presumably from about 100 to 1000 or more glucose amine units in length. However, it is impossible at the present state of our knowledge to fix definite lengths for these chains any more than it is possible to fix definite chain lengths for derivatives known as substantially undegraded cellulose.

75 80 Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. Process for the manufacture of substantially undegraded, at least partially deacetylated chitin, which comprises treating chitin, preferably under limited access of air, with 5% to 55% aqueous

- caustic alkali at a temperature not exceeding 150° C., until the product is soluble in dilute aqueous acetic acid to give solutions which, at a concentration of 2.5 parts of product per 100 parts of dilute aqueous acetic acid, have a viscosity greater than 1 poise at 25° C.
5. Process according to claim 1 which comprises heating chitin, preferably under limited access of air, with 40% to 10 50% aqueous sodium hydroxide for 1 to 6 hours at 110° C. to 115° C.
10. Process according to either of the preceding claims in which the treatment is continued until from 0.2 to 0.9 of the 15 acetyl groups have been removed and 0.2 to 0.9 free amino groups per C<sub>6</sub> unit have been formed.
15. Substantially undegraded, at least 20 partially deacetylated chitin whenever prepared in accordance with the process of any of Claims 1—3, or by the obvious chemical equivalent of such process.
5. Process of preparing useful solutions of substantially undegraded, at least 25 partially deacetylated chitin which comprises reacting deacetylated chitin as claimed in Claim 4 with an acid to form a salt thereof and simultaneously or successively forming an aqueous solution 30 of said salt.
6. Process of modifying the viscosity of the solutions obtained as claimed in Claim 5 by use of an oxidising agent substantially as described.
35. 7. Process for making aqueous solutions of augmented viscosity of salts of substantially undegraded, partially deacetylated chitin as claimed in Claim 5 which comprises the step of first heating the carbohydrate polymer itself in the dry state.

Dated the 21st day of June, 1935.

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Abingdon : Printed for His Majesty's Stationery Office, by Burgess & Son.

[Wt. 8138.—50/11/1939.]